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METHOD FOR PRODUCING ION EXCHANGER
[ION KOKANTAI NO SEIZO HOHO]

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Specification

1. Title of the Invention

Method for Producing Ion Exchanger

2. Scope of Patent Claims

1) A method for producing an ion exchanger, characterized in that an oxidatively polymerizable monomer is polymerized in an ion exchanger which contains an oxidizing agent.

3. Detailed Description of the Invention

(Industrial Applicability)

The present invention relates to a method for producing an ion exchanger, wherein an oxidatively polymerizable monomer is polymerized in an ion exchanger which contains an oxidizing agent.

(Prior Art and its Problem)

Conventionally, various attempts have been made to adjust the function of the ion-exchange membrane, such as improving or restricting the ion-selective permeability, and modifying the selective permeability between ions with the same sign. Further, another attempt which has been made to impart an additional function to the ion-exchange membrane is to impregnate a polymerizable vinyl monomer in a cation-exchange membrane or anion-exchange membrane so as to be polymerized, thereby achieving a reduction in the diffuse transmission rate of salts,

the improvement in the transport number, the reduction in the amount of the acid leakage, and the reduction in the base leakage. However, in general, these methods often include a process of polymerizing a vinyl monomer in a membrane, which results in the ion-exchange membrane swelling by the influence of the vinyl monomer. Therefore, the reduction in the mechanical strength of the membrane is induced. In addition, there has been a report about condensing a condensation-type monomer in an ion-exchange membrane; however, in many cases, this process requires a heat treatment in order to complete the condensation reaction, resulting in the properties of the membrane becoming compromised.

(Means of Solving the Problems)

In view of the above-described situation, the present inventors conducted intensive research in order to modify the properties of an ion exchanger and impart additional functions to the ion exchanger by generally forming a matrix of a different polymer in the matrix of the ion exchanger. As a result, the present inventors discovered that a heterocyclic compound, such as pyrrole and a derivative thereof, and thiophene and a derivative thereof, had high affinity for an ion exchanger and was relatively readily polymerized in the membrane by an oxidative reaction, thereby modifying the properties of the ion exchanger and

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providing an ion exchanger having additional functions. The present invention has thus been completed. More specifically, the present invention provides a method for producing an ion exchanger which is characterized in that an oxidatively polymerizable monomer is polymerized in an ion exchanger which contains an oxidizing agent.

As the ion exchanger according to the present invention, not only organic ion exchangers but also inorganic ion exchangers themselves, such as zirconium phosphate, and inorganic ion exchangers which have been formed by being molded by the application of pressure or heat with the aid of a suitable organic or inorganic binder can be preferably used. Preferred examples of organic ion exchangers include polymerizable ion exchangers, such as so-called styrene-divinyl benzene copolymers to which an ion-exchange group is bonded, and condensation type ion exchangers to which a cation-exchange group and/or an anion-exchange group are bonded. Both conventional homogeneous and heterogeneous ion exchangers can be used as the ion exchanger according to the present invention. Further, the substrates for the ion exchanger for the present invention are not restricted but any types can be used, such as hydrocarbon types, fluorocarbon types and perfluorocarbon types.

Further, the ion exchangers that can be used in the present invention are not particularly restricted as long as an ion

exchange group is bonded to the ion exchanger in an amount of from 0.1 meq to 15 meq per 1 g of the ion exchanger on dry basis. Preferred examples of ion exchange groups include conventional cation-exchange groups, such as sulfonic acid, carboxylic acid, phosphoric acid, phosphorous acid, sulfonic acid esters, phenolic hydroxyl groups, thiol groups, and tertiary perfluoroalcohols, and conventional anion-exchange groups, such as primary, secondary and tertiary amines, and onium bases, such as quarternary ammonium, tertiary sulfonium, quarternary phosphonium, and cobalticinium.

Further, of the above-enumerated ion exchangers, preferred examples of ion exchangers that can be suitably used according to the intended use include those where the diffusion of the ion-exchange groups is uniform, those where the diffusion of the ion-exchange groups is biased, and those which have a concentration gradient. Ion-exchange groups which are present in the ion exchanger may consist of only cation-exchange groups, only anion-exchange groups, or both ion-exchange groups. In the case where both ion-exchange groups are present in the ion exchanger, the ion-exchange groups can be present in two or more layers and can also be uniformly present in the ion exchanger. Further, various ion exchangers are formed by various present states of ion-exchange groups, such as a layer structure consisting of a layer of cation-exchange groups, a layer of both

cation-exchange groups and anion-exchange groups, and a layer of cation-exchange groups or a layer of anion-exchange groups, or the reverse structure, and ion exchangers in any of the above-described forms can be effectively used in the present invention. The terms "cation-exchange groups" and "anion-exchange groups" refer not only to the same cation-exchange groups and anion-exchange groups, but cation groups can consist of dissimilar cation-exchange groups, such as carboxylic acid and sulfonic acid. In many cases, the use of dissimilar groups provides a particularly preferred result. Further, it is not necessary for the inorganic ion exchanger and the organic ion exchanger to have their own matrix, but a complex of both ion exchangers can also be preferably used. Specific examples of such complexes of ion exchangers include an ion exchanger which is obtained by molding fine powder of an inorganic ion exchanger with the aid of a thermoplastic organic ion exchanger into a suitable shape, and an ion exchanger which is obtained by dissolving a high polymer electrolyte or an inert polymer in a suitable solvent, and diffusing an inorganic ion exchanger therein in order to disperse the solvent, thereby obtaining an ion exchanger having a desired shape. In addition, the ion exchanger used in the present invention is not restricted to a membrane, but can be present in various forms, such as particles, powder, fibers and tubes.

In the present invention, by using the above-described various ion exchangers, and by further using oxidizing agents and oxidatively polymerizable monomers, which are described later, various effective ion exchangers having improved properties can be obtained. The perspective embodiments of such ion exchangers are described in the following. Examples of the embodiments are as follows:

(1) By using a cationic oxidizing agent against an anion exchanger and using an anionic oxidizing agent against a cation exchanger in order to utilize the characteristic in which it is difficult for the oxidizing agents to be evenly added to the respective ion-exchangers, an oxidatively polymerizable monomer can be readily polymerized on one side,

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thereby obtaining an ion exchanger having an asymmetric structure. (2) In contrast, in the case where both ion exchangers are used, since both cationic and anionic oxidizing agents can be evenly added, an ion exchanger having a uniform structure can be readily obtained by polymerizing the resulting oxidatively polymerizable monomer. (3) Further, in the case where a bipolar ion-exchange membrane is used, since an oxidatively polymerizable monomer can be polymerized on one side of the membrane, a membrane of the polymer in which an electroconductive layer and an insulating layer are alternately

laminated can be obtained. (4) In the case where a hydrocarbon-type ion-exchanger having a crosslinked structure is used, since the impregnation rate and amount of the oxidatively polymerizable monomer can be easily controlled, the mechanical strength of the resulting ion exchanger can be easily maintained. In particular, in the case where an ion exchanger having a crosslinked structure and a reinforcing material, the resulting ion exchanger has more improved mechanical strength.

In the present invention, as the oxidizing agent to be present in the ion exchanger, any conventional oxidizing agents can be used without particular limitation. Examples of such oxidizing agents include: peroxides, such as H_2O_2 and $(C_6H_5CO)_2O_2$; metal salts, such as $FeCl_3$, $CuSO_4$, $CuCl_2$ and $RuCl_3$; peroxo acids (salts), such as $Na_2S_2O_8$, N_2SO_5 and $(NH_4)_2SO_5$; and oxoates, such as $NaClO$, $NaBrO$ and $NaClO_3$. Specific examples include: metal ions, whose charge can be changed by the oxidation reduction, such as trivalent iron ion, divalent copper ion and trivalent ruthenium ion; organic compounds whose charge can be changed by the oxidation reduction; cations, such as metallic complex cations; and anions having oxidizability, such as persulfate ion and perchlorate ion. These cations and anions in the oxidation state exchange ions with the ion-exchange groups of the ion exchanger and are therefore uniformly diffused in the ion exchanger, which is preferred. When the oxidation polymerization according to the

present invention is conducted on only the surface layer of the ion exchanger, a peracid to which a long-chain alkyl is bonded or a compound to which a peracid group is bonded, said compound having a structure, such as a naphthalene ring, which does not enter the pores of the ion exchanger can be used.

Examples of oxidatively polymerizable monomers that can be used in the present invention include: pyrrole and derivatives thereof, such as N-methyl pyrrole, 2-ethyl pyrrole; thiophene and derivatives thereof; isothianaphthene and derivatives thereof; and others, such as indole, azulene, furan, aniline, phenol, benzene, naphthalene and derivatives thereof. In particular, heterocyclic compounds, such as pyrrole, indole, azulene, thiophene, furan and derivatives thereof, can be preferably used because these oxidatively polymerizable monomers have high affinity for the ion exchanger and can therefore be readily oxidatively polymerized in the ion exchanger.

Methods for the oxidation polymerization in the present invention are not particularly restricted, but the oxidation polymerization can be generally conducted by impregnating an ion exchanger containing an oxidizing agent in an organic solvent, such as acetonitrile and ethyl alcohol, or an inorganic solvent, such as water to which an oxidatively polymerizable monomer is dissolved or dispersed. The impregnation is conducted by cooling the ion exchanger in a temperature range where the solvent is

not frozen or by heating the ion exchanger in a temperature range where the solvent is not boiled. Further, in the process of polymerization, the concentration of the monomer is not particularly restricted, but can be in a range of from 0.01% to saturation. Alternatively, the monomer can be polymerized in the suspension state. The polymerization time may vary depending on the type of the monomer used and the type of the ion exchanger used, but can be suitably selected from a range of from 1 minute to 72 hours.

(Operation and Effect of the Invention)

The ion exchanger obtained by the present invention has a varied ion-selective permeability, particularly the selective permeability between ions with the same sign, whereby the permeation of ions having large charge and ions having a small hydrated ion diameter can be generally prevented. Depending on the oxidation polymerization method for the monomer, an electron conductive function is provided, whereby the ion-exchange membrane can be modified into a novel functional material, such as a sensor.

Some of the specific examples of such a functional material are described below.

(1) A cation-exchange membrane which had been crosslinked with a styrene-divinyl benzene copolymer was dipped in an aqueous solution of iron chloride so as to be formed into an iron-type

cation-exchange membrane. When the resulting membrane was thoroughly washed with water and was then dipped in an aqueous solution containing pyrrole, pyrrole was polymerized while cation exchange was occurring. The resulting membrane was thoroughly washed with water, was then sufficiently conditioned with 1 N hydrochloric acid and 0.5 N salt solution in order to remove Fe^{++}. When the solution containing 0.25 N hydrochloric acid and

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0.25 N salt solution was subjected to electrodialysis, hydrogen ions selectively permeated.

(2) After the membrane obtained in the step (1) was dried under reduced pressure, the electric conductivity was measured, and the membrane had an electric resistance of 1 $k\Omega\text{-}cm^2$ or less. In contrast, the membrane in which pyrrole was not polymerized had an electric resistance of 20 $M\Omega\text{-}cm^2$ or more.

(3) An anion-exchange resin having a pyridinium salt group as an anion-exchange group was equilibrated with an ammonium persulfate solution so as to be formed into a persulfate ion type anion-exchange resin. When the resulting anion-exchange resin was dipped in an aqueous solution of pyrrole, the pyrrole was selectively adsorbed and caused ion exchange with the anion-exchange membrane and was then polymerized. Pale yellow

spherical resins were turned black, but were not eluted even when the resin were repeatedly washed with an acid and an alkali.

(4) A tubular ion-exchanger having a benzyl trimethyl ammonium ion as an anion-exchange group was equilibrated with an ammonium persulfate solution so as to be formed into a persulfate ion type anion-exchange resin. When the resulting anion-exchange resin was dipped in an aqueous solution of aniline, the aniline was impregnated and polymerized in the anion exchanger, and the pale yellow tubular ion exchanger turned black. When the electric conductivity was measured, the ion exchanger had an electric resistance of 100 Ω-cm^2 or less while the ion exchanger without aniline had an electric resistance of 20 MΩ-cm^2 or more.

(5) A pyridinium salt group-type anion exchange membrane was dipped in an aqueous solution of ammonium persulfate in order to cause ion exchange of the anion exchange group with the perfulfate ion, and aniline was further added thereto so as to cause polymerization. As a result, the aniline was polymerized in the aqueous phase so as to be formed into a polyaniline having a black color and was then impregnated and polymerized in the membrane. When the membrane was collected in order to measure the selective permeability of sulfuric acid ion and chlorine ion, in the case where polyaniline was not present, when 1 equivalent weight of chlorine ion permeated, 0.3 equivalent weight of the sulfuric acid ion permeated. In

contrast, in the case where polyaniline was impregnated, 0.01 equivalent weight of sulfuric acid ion permeated.

(Embodiments)

The present invention is described in greater detail below with reference to embodiments, but is not restricted thereto in any way.

Embodiment 1

A cation-exchange membrane ($7.0 \times 7.0\ cm^2$) which was a membrane to which a sulfonic acid group was bonded and which had an ion exchange capacity of 2.3 meq/g dry membrane was dipped in an aqueous solution of 5% ferric chloride so as to be equilibrated, thereby obtaining a ferric ion type cation-exchange membrane. Subsequently, the resulting membrane was dipped in 500 cc of an aqueous solution of 2% pyrrole and was stirred. Once the resulting solution had been allowed to stand for 16 hours, the resulting membrane was washed with water and ethanol and was then dipped in 1 N hydrochloric acid, with the hydrochloric acid being repeatedly replaced. When the absorption of iron was observed by the fluorescent X-ray analysis, iron was found to be almost completely removed.

An acrylic cell which had been divided into two compartments each having an internal volume of 120 cc by the resulting membrane was filled with 0.25 N NaCl and 0.25 N $CaCl_2$, respectively. Before the membrane was installed into the cell

having two compartments, the membrane was sufficiently equilibrated with 0.25 N NaCl and 0.25 N $CaCl_2$, respectively. A silver electrode and a silver chloride electrode were provided into respective compartments in the cell in order to conduct electrodialysis at a current density of 1 A/dm^2 through the electrodes. The effective conduct area was 0.1 dm^2. When the amount of cation which had permeated through the membrane 2 hours after conduction was measured, the current efficiency was 97%, and the amount of Ca^{2+} which had permeated through the membrane in the case where 1 equivalent weight of Na^+ had permeated through the membrane was 0.2 equivalent weight.

On the other hand, when a conventional sulfonic acid type cation-exchange membrane in which pyrrole had not been impregnated and polymerized was used as a comparative example and was subjected to electrodialysis under the same conditions, the current efficiency was 98%, and the amount of Ca^{2+} which had permeated through the membrane in the case where 1 equivalent weight of Na^+ had permeated through the membrane was 2.1 equivalent weight.

In addition, when the membrane in which pyrrole had been impregnated and polymerized and which had been subjected to electrodialysis was collected, and was then equilibrated with 1 N hydrochloric acid, was dried under reduced pressure, and subjected to the measurement of electric conductivity, the

resulting electric resistance was 28 Ω-cm^2. In contrast, when the cation-exchange membrane without pyrrole was subjected to the measurement of electric conductivity under the same conditions, the resulting electric resistance was 20 MΩ-cm^2 or more.

Further, the cation-exchange membranes used in the present embodiment were obtained by copolymerizing styrene and divinyl benzene, with the proportion of the divinyl benzene being 5%. The measurement of electric conductivity was conducted by applying silver paste to a membrane having a width of 1 cm at intervals of 1 cm, drying the coating film, conducting the measurement with an electric conductivity meter, and calculating the specific conductance based on the conversion of membrane thickness.

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The same applies to the following embodiments.

Embodiment 2

Fine powder of polyvinyl chloride was added to a mixture of ethylene, divinyl benzene and 4-vinyl pyridine, and the resulting mixture was further mixed with benzoyl peroxide as a polymerization initiator in order to obtain a viscous paste-like mixture. The resulting mixture was applied to a cloth which was constituted of polyvinyl chloride. Both surfaces of the resulting cloth were covered with cellophane. The resulting cloth was thermally polymerized at a temperature of 70 degrees

Celsius in a nitrogen atmosphere, thereby obtaining a polymer membrane. The resulting polymer membrane was dipped in an alkylated bath containing a mixture solution which was constituted of hexane and methyl iodide at a temperature of 25 degrees Celsius for 24 hours, thereby obtaining an anion-exchange membrane having a quarternary ammonium salt group as an anion-exchange group.

The resulting anion-exchange membrane was dipped in an aqueous solution of 10% ammonium persulfate so as to be modified into an ammonium persulfate type ion-exchange membrane, and the resulting ion-exchange membrane was dipped in an aqueous solution of 5% aniline and was stirred therein at room temperature for 8 hours. The membrane which had pale yellow color turned black.

When the resulting membrane was collected, was conditioned with 1 N hydrochloric acid and 0.5 N ammonia water, an electrodialysis was conducted with a 1:1 mixture solution of 0.25 N salt cake and 0.25 N of common salt in order to compare the membrane permeability of SO^{4--} and Cl^- by the same method as in Embodiment 1. As a result, in the case of the membrane without aniline, the amount of SO^{4--} which had permeated through the membrane was 0.3 equivalent weight per 1 equivalent weight of Cl^-, whereas in the case of the membrane in which aniline had

been polymerized, the amount of SO^{4--} which had permeated through the membrane was only 0.01 equivalent weight.

Further, when the anion-exchange membrane in which aniline had been impregnated and polymerized after electrodialysis was dried under reduced pressure and was then subjected to the measurement of electric conductivity, the resulting electric resistance was 12 Ω-cm^2.

Embodiment 3

A paste-like mixture obtained by adding fine powder of polyvinyl chloride to a mixture of styrene, 4-vinyl pyridine, and divinyl benzene was mixed with benzoyl peroxide. The resulting mixture was applied to a cloth which was constituted of polypropylene and was thermally polymerized, thereby obtaining a membrane. The resulting membrane was dipped in 97% sulfuric acid for 3 days so as to be gradually sulfonated. Next, the resulting membrane was first dipped in 0.1 N caustic soda and was then dipped in a bath containing hexane and methyl iodide in order to alkylate the pyridine ring. The cation exchange capacity of the resulting ion-exchange membrane was 0.81 meq/g dry membrane and the anion exchange capacity was 1.12 meq/g dry membrane. With the ion-exchange membrane, the following two processes were conducted.

(a) The membrane was dipped in an aqueous solution of ruthenium trichloride so as to be modified into a ruthenium ion type

membrane. When the resulting membrane was washed with water and was dipped in an aqueous solution of 2% pyrrole, pyrrole was impregnated and polymerized in the ion-exchange membrane. The resulting membrane was washed with water and methanol, was dried under reduced pressure, and was subjected to the measurement of electric conductivity. The resulting electric resistance was 25 $\Omega\text{-cm}^2$.

(b) The membrane was dipped in an aqueous solution of 5% sodium persulfate so as to be modified into a persulfate ion type membrane. The resulting membrane was dipped in an aqueous solution of 1% aniline under stirring so as to be polymerized. The membrane was washed with water and methanol, and was then dried under reduced pressure. The resulting membrane had an electric resistance of 19 $\Omega\text{-cm}^2$.

Further, when both membranes were subjected to electrodialysis with a 1:1 mixture solution of 0.25 N hydrochloric acid and 0.25 N of common salt, the membrane in which pyrrole had been impregnated and polymerized had a current efficiency of 95% and allowed 21 equivalent weight of hydrogen ion to permeate per 1 equivalent weight of Na^+. Further, the membrane in which polyaniline had been impregnated and polymerized had a current efficiency of 97% and allowed 30 equivalent weight of hydrogen ion to permeate per 1 equivalent weight of Na^+.

Embodiment 4

Styrene, butadiene and N,N′-dimethyl vinyl benzyl amine were subjected to a living aniline polymerization in order to synthesize a block copolymer. The resulting mixture was cast into a flat plate in order to obtain a film. When the resulting film was observed through an electron microscope, a phase-separated structure was found to be formed. More specifically, the structure was divided into the region of styrene, the region of butadiene and the region of N,N′-dimethyl vinyl benzyl amine. The resulting film was sulfonated by using sulfuric acid in order to introduce a sulfonic acid group, was then substituted with methanol, and was treated with methyl iodide in order to introduce a quaternary ammonium salt group. The resulting membrane in which the region of cation-exchange group, the neutral region, and the region of anion-exchange group were distributed as a mosaic was dipped in an aqueous solution of iron trichloride in order to exchange the iron ion with

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the cation-exchange group. Next, the membrane was dipped in an acetonitrile solution of 2% pyrrole, the pyrrole was impregnated in the region, in which the sulfonic acid group was present primarily, and was then oxidatively polymerized.

When the permeability of common salt and sucrose was measured by using the resulting membrane, in the case of the

membrane in which pyrrole had not been impregnated so as to be oxidatively polymerized, the coefficient of permeability of sucrose was 1/81 that of common salt, whereas in the case of the membrane in which pyrrole had been impregnated so as to be oxidatively polymerized, the coefficient of permeability of sucrose was reduced to 1/210. Further, when another membrane which had been prepared by the same method was washed with water and methanol and was then dried under reduced pressure in order to measure the electric conductivity, while the electric conductivity in the thickness direction was confirmed, the electric conductivity in the two-dimensional direction was not confirmed, which indicates that the resulting membrane was an anisotropic conductive membrane.

Embodiment 5

A viscous paste-like mixture was prepared by mixing polyethylene fine powder with a mixture of styrene and divinyl benzene. The resulting mixture was applied to a polypropylene cloth, and only one side of the membrane was sulfonated by concentrated sulfuric acid in a reaction apparatus in order to introduce a sulfonic acid group into the reacted side. Next, when the resulting membrane was dipped in an aqueous solution of 5% ruthenium trichloride and was then dipped in an ethyl alcohol solution of 10% pyrrole for 16 hours, the pyrrole was impregnated only in the region of sulfonic acid group and was

then oxidatively polymerized. When the resulting membrane was washed with water and methanol and was then dried under reduced pressure in order to measure the electric conductivity, the electric conductivity in the two-dimensional direction was confirmed only on one side of the membrane while the back side was an insulating material.

Embodiment 6

The membrane, one side of which had been sulfonated in Embodiment 5, was installed in the reaction apparatus in which one side of the membrane could be reacted, and the unreacted side of the membrane was brought into contact with a carbon tetrachloride solution of chloromethyl ether and tin tetrachloride in order to introduce a chloromethyl group into one side of the membrane. Next, the resulting membrane was dipped in a water-acetone solution of trimethylamine so as to be aminated, thereby obtaining a membrane, one side of which had a sulfonic acid group and the other side of which had a quarternary ammonium salt group. The resulting membrane was dipped in an aqueous solution of 5% sodium persulfate in order to modify the region of the anion-exchange group into a perfulfate ion type, and was then dipped in an ethanol solution of 5% aniline. 10 hours later, aniline was polymerized in the region of the anion-exchange group. The electric conductivity was observed in the region.

Next, the resulting membrane was dipped in an aqueous solution of 5% iron chloride in order to cause ion exchange of the cation-exchange group with iron ion, was washed with water, and was then dipped in an ethanol solution of 2% pyrrole. As a result, pyrrole was polymerized in the region where the cation-exchange group was present. When the electric conductivity of the membrane after being washed with water and dried under reduced pressure; the electric conductivity was confirmed on the side where the polymerization had been caused.

Embodiment 7

Commercially available cation-exchange resin, anion-exchange resin and ion-exchange resin were subjected to the following treatments.

(a) A sulfonate type cation-exchange resin was equilibrated with an aqueous solution of iron chloride, was then dipped in an aqueous solution of 10% pyrrole, and was allowed to stand. As a result, the cation-exchange resin having a slightly brown color turned black and was polymerized.

(b) A resin having a quarternary ammonium salt group type anion-exchange group was dipped in an aqueous solution of 10% ammonium persulfate, was then dipped in an ethanol solution of aniline, and was allowed to stand. As a result, a black spherical resin was obtained.

(c) A spherical ion-exchange rein having a quarternary ammonium salt group and a sulfonate group was dipped in an aqueous solution of 5% iron chloride and was then dipped in an aqueous solution of pyrrole. As a result, the resulting black spherical resin turned black and pyrrole was oxidatively polymerized.

All of the above resins a), b) and c) which had been dried under reduced pressure were found to have electric conductivity.

Embodiment 8

Polychloromethyl styrene was extruded from a nozzle in order to obtain a tubular polymer. The resulting polymer was brought into contact with a carbon bisulfide solution of aluminum chloride and a crosslinkage was formed by using Friedel-Crafts acid. Next, the resulting polymer was dipped in a mixture solution of trimethylamine, water and acetone so as to be aminated, thereby obtaining a tubular anion-exchanger having a quarternary ammonium salt group. The resulting polymer was equilibrated with an aqueous solution of ammonium persulfate and was then dipped in an aqueous solution of pyrrole.

When the electric conductivity of the resulting tube was measured,

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while the tube in which pyrrole had not been polymerized had no electric conductivity, the tube in which pyrrole had been polymerized had electric conductivity.

Embodiment 9

Fine powder of cation-exchange resin obtained by sulfonating a styrene-divinyl benzene copolymer was mixed with polyethylene. The resulting mixture was extruded from a nozzle by the same method as in Embodiment 8, thereby obtaining a tubular cation-exchanger. The resulting tubular cation-exchanger was boiled in purified water, was then dipped in an aqueous solution of iron trichloride so as to be modified into an iron type, was then dipped into an aqueous solution of 2% thiophene, was heated at a temperature of 50 degrees Celsius and was then allowed to stand for 24 hours. Next, the tubular ion exchanger was collected, was washed with water, and was dried under reduced pressure. When the electric conductivity was measured, the ion exchanger was found to have electric conductivity.